IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	: Kumar et al.	
Applic No.:	09/085,514	
Filed	: May 27, 1998	Group Art Unit: 1773
For	: SILICON OXIDE PARTICLES	Examiner: K. Bernatz
Docket No.:	2950.02US01	

DECLARATION UNDER 37 C.F.R. § 1.132

Assistant Commissioner for Patents
Washington, D.C. 20231

I HEREBY CERTIFY THAT THIS PAPER IS BEING SENT BY U.S. MAIL, FIRST CLASS, TO THE ASSISTANT COMMISSIONER FOR PATENTS, WASHINGTON, D.C. 20231, THIS

_____ DAY OF _____, 20___.

_____
PATENT ATTORNEY

Sir:

I, Rajiv K. Singh, Ph.D., hereby declare as follows:

1.   I am presently a Professor of Material Science and Engineering at the University of Florida at Gainesville. Apart from my academic responsibilities, I provide consulting services through R. K. Singh Consulting Inc.

2.   I received my Ph.D. degree in 1989 in Material Science and Engineering from North Carolina State University, Raleigh, NC.

3.   I have been on the faculty at the University of Florida since 1990. I was promoted to Associate Professor with tenure in 1995 and to full Professor in 1997. A copy of my Curriculum Vitae is attached.

4.   My recent accomplishments include receiving a National Science Foundation Young Investigator Award in 1994 and the Hardy Gold Metal for Outstanding Contributions in Material Science in

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1995. I was a Distinguished Visiting Professor/Scientist at National University of Singapore (1999) and National Institute for Materials and Chemical Research, Tsukuba, Japan (2000). I am a fellow of the American Society for Materials (ASM). I am the author or co-author of more than 300 scientific articles and conference proceedings. I have co-edited seven books and guest edited five journal issues.

5. I have organized over 15 international conferences in advanced processing of materials including nano-particle science and technology and chemical- mechanical polishing (CMP).

6. I have been the Associate Director of the Engineering Research Center for Particle Science and Technology, at the University of Florida from 1994 -2001. My prime responsibility at this position was to develop advanced techniques for characterization of particles.

7. I am under a Consulting Agreement with NanoGram Corporation to provide consulting services in the area of chemical-mechanical planarization. I am not a shareholder in NanoGram Corporation. Also, I have no interest in the present patent application.

8. I have been working in the area of surface polishing and material science relating to properties of inorganic particles for many years. My laboratory at the University of Florida has performed extensive experiments in particle properties and in surface polishing.

9. I have read carefully U.S. Patent 5,128,081 to Rostoker, U.S. Patent 5,128,281 to Siegel et al., U.S. Patent 5,846,310 to Noguchi et al., U.S. Patent 4,775,520 to Unger et

al., and a passage from Ullmann's Encyclopedia of Industrial Chemistry, Vol. A23 at pp. 635-639. In addition, I have read the pending claims of the above noted patent application entitled "SILICON OXIDE PARTICLES." I did not participate in any capacity with the preparation of the SILICON OXIDE PARTICLES patent application.

10.   With respect to the Rostoker '081 patent, a theoretical type of distribution is described in the patent. This distribution as described by Rostoker has several internal inconsistencies, as described below. Additionally, this distribution described by Rostoker does not conform to any standard representation of distribution functions described in standard textbooks and standard references.

In the Rostoker distribution, X is the average particle size. Y relates to a range around X. However, Q is important since Q, in principle, defines the size distribution. Unfortunately, the discussion of Q is not internally consistent. Q is indicated in the patent to be a dimensionless quantity. Q is defined as the concentration of particles at "X" divided by a concentration of particles in a range 3dB lower than "X". The numerator of this expression has units of $\#/cm^3$, whereas the denominator term denoted by concentration of particles in a range of sizes 3dB below X has units of $\#/cm^2$. Thus, according to Rostoker's definition, Q is not dimensionless but has units of 1/cm or 1/length. For Q to be a dimensionless quantity, either both the quantities should be defined in a certain range (e.g., concentration range +1dB of X divided by concentration at range +1dB at X/2), or both the quantities should describe the concentration at specific values (e.g., at X and at 3dB below X).

Even if we assume that the patent described Q as ratios at concentrations at X and at 3dB below X (which is not the case

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in the patent description), which makes Q dimensionless, there are several more inconsistencies. First, the particle size distribution is defined by only two points, which can be extrapolated into any distribution one might choose to elect. Secondly, if we define A as the point at which the concentration of particles in a range 3bd below x, then the concentration at A equals concentration at $X/10^{0.3}$. Then the concentration at A corresponds approximately to the concentration at X divided by 2. This value does not correspond to a Gaussian distribution, and the evaluation of A does not address the problems with the definition of Q. The Rostoker patent nowhere describes a 3 sigma (standard deviation) distribution. Also, the standard deviation cannot be defined for a distribution given in the patent.

It should be noted that the particle size distribution, as described in the Rostoker patent is not consistent with the particle size distributions that are frequently used in the standard particle size and technology books and publications. Examples of some of the standard book publications with which I am familiar are 1) A. Jillaventesa, S. Dapkunas and L.H. Lum, "Particle Size Characterization," NIST Recommended Practice Guide, NIST Special Publication, 960-1 (2001); 2) T. Allen, "Particle Size Measurement," 4th Edition, Chapman and Hall, London (1992); 3) B. H. Kaye and R. Trottier, Chemical Engineering, 99:84 (April 1995); 4) R. J. Hunter, "Foundations of Colloidal Science," Wiley (1998); 5) E. Kissa, "Dispersions, Characterization Testing and Measurement," and 6) B. V. Miller and R. Lines, CRC Critical Reviews in Analytical Chemistry, 20:75-116 (1988). Relevant pages from Reference 4 are attached.

The only source of powders described in the Rostoker '081 patent is the process described in the Siegel patent. However, the Siegel patent only describes the formation of nanocrystalline materials. In other words, the materials are polycrystalline materials with nanocrystalline domains. The

Siegel patent does NOT describe the formation of submicron particles. Furthermore, I am aware of no approaches for the formation of silica particles as claimed by NanoGram except for the NanoGram process, as described further below.

11.   With respect to the Unger '520 patent, this patent describes the formation of a silica gel using a two-step process. I have considerable experience with reactions that form silica gels including the Stober process and processes similar to the Unger process, from work that has been performed in my lab in Gainesville. Also, the process that leads to the formation of silica particles from alkoxide precursors is well documented in the literature, such as the texts Sol Gel Science, by C. Jeffrey Brinker and G. Scherer, Academic Press (1990) and The Chemistry of Silica, by R. K. Iler, Wiley (1979). The first step in the Unger process uses the Stober process to form a silica gel.

In the second step, increasing the particle size and removal of the porosity further refines the sol. In both the Stober and Unger processes, the hydrolysis of the alkoxide precursors occurs in basic conditions leading to formation of sol as a result of hydrolysis, polymerization and condensation reactions. The sol particle in this process typically consists of partially coalesced small clusters that form porous structures. The clusters typically are made of trimers and tetramers of silicon-hydrogen-oxygen precursors such as $SiO(OH)_3$, $SiO_2(OH)_2$, $Si_4O_6(OH)_6$, $Si_4O_8(OH)_4$, etc. After the condensation process, the clusters contain a large number of silanol groups and siloxane bonds. Several workers have made extensive studies on the use of FTIR, NMR and Raman Spectroscopy to understand the formation of the particles. Articles by Lippert et al. and Zerda et. al. are attached.

The cluster-like aggregates making the sol particles are typically smaller than 50 nm, and have a high surface area due to formation of the porous structures. Because of the high

porosity the surface area of the sols are much larger than the theoretical calculated surface area. The Unger patent also shows that the surface area of the sols of 100 – 350 m^2/gm, which is typically nearly two orders of magnitude greater the theoretically calculated surface areas based on the size of the particle measured by standard techniques such as TEM, and light diffraction measurements. Thus the sols are chemically and structurally different from a non-porous silica particle which is typically obtained from the Nanogram process. Specifically, the sols may have significant chemical variation than silicon dioxides, and the aggregates do not have the uniformity described in the NanoGram claims.

12. With respect to the Noguchi patent, this patent describes the application of a coating onto the silica gel of the Unger patent. The Noguchi patent does not deal with the synthesis of silica particles.

13. Pyrolytic or flame produced process is a standard method to make small particles of silica, alumina, titania, etc. There are several references that show the details on the flame-produced process. Examples include 1) Ulmann's encyclopedia; 2) Ulrich, Combustion Science Tech. 4:47-57 (1971); 3) G. W. Scherer in Better Ceramics Through Chemistry, eds. C. J. Brinker et al. (North Holland, NY 1984); 4) D. W. Schaefer, Material Research Society Bulletin, 13:22-27 (1988); 5) J.E. Martin et al., Phys. Rev. A 33:3540-3543 (1986); 6) A. J. Hurd et al., Phys. Rev. A 35:2361-2364 (1987); 7) J. D. F. Ramsay, Colloidal Surfaces 18:207-221 (1986). Copies of References 2, 5 and 6 are attached for reference. In the flame oxidation process, the small particles, which are formed by the oxidation reaction initially aggregate with each other by a ballistic process which mean that the mean free path of the aggregating species is large, compared

to the cluster size. In the second phase of the growth process, once the particles are large compared to the mean free path the trajectories of the particles change from ballistic to Brownian motion. The meandering path of the Brownian motion encourages attachment of the incoming cluster to the target periphery reacting aggregates and ramified fractal structures. Standard techniques such as visible light scattering and small angle neutron scattering have been used to show that the fractal dimension of the particles is characteristic of the diffusion limited cluster aggregation. Depending on the residence time and reactor design, the size of the primary particles may vary from 20 nm to 200 nm.

Although the primary particle size of the pyrolytic silica can be small, the particles form hard aggregates that neck in the aggregates, which make them difficult to disperse. The neck formation has been determined from transmission electron micrography (TEM). Attempts to disperse these particles result in dispersion of clusters of the fused aggregates forming individual particles. There is no way to separate the fused aggregates because the fusing results in hard bonding. Workers in field unfortunately refer to the grains that are fused together as primary particles, even though the hard fusing of these <u>grains</u> prevents separation of the grains as distinct particles. The actual particles are the fused entities or cluster rather than the individual 'grains. Thus, the particles are very non-uniform even if they are formed from fused grains that may be relatively uniform.

As further support for observations from my direct experience, I have attached a TEM micrograph from my lab that provide documentary evidence of these materials formed by the process described in Ullmann's Encyclopedia. The particle have an average particle size of about 20 - 50 nm and cluster sizes on average of about 250 nm. Due to the hard fusing of these

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particles, the aggregates do not have high uniformity.

14.   In my experiences, I have not seen materials comparable to the materials claimed in the NanoGram patent application. Based on my extensive experience with surface polishing, I expect that the NanoGram materials will be very good materials for surface polishing since the performance is expected to depend on the uniformity of the polishing materials. Thus, the NanoGram silica particles fill a void in the types of materials available for surface polishing. While NanoGram has not commercially exploited their silica materials for surface polishing yet due to their efforts with other commercial activities, I expect that these materials will someday have a significant commercial role in improving surface polishing of substrates.

14.   I declare that all statements made herein that are of my own knowledge are true and that all statements that are made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: _Dec. 10 '01_   By: _Rajiv K. Singh_
                                  Rajiv K. Singh, Ph.D.